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Technical Report Summary

↙ This research was undertaken to help in the development of more efficient and scalable visible and ultraviolet lasers. The goal of the project seeks to determine whether transfer of energy from high vibrational levels of diatomic molecules can occur to lasing electronic states and if this transfer can be used to produce visible-UV lasers. In general, very little is known about vibration-to-electronic energy transfer. We cannot successfully predict and, at present, have not developed lasers based on such transfer. The concept is extremely attractive, if attainable, because there are numerous means of efficiently generating high vibrational excitation in molecules.

Our research effort explored the details of a simple system involving transfer of vibrational excitation from H_2 to the electronic state of Br atom ($^2P_{1/2}$). Although some transfer was observed, sufficient excitation was not achieved in the Br atom to produce lasing. It was found that in several cases, excitation of Br occurred by electronic-to-electronic excitation transfer. From this study and our further studies on the excitation of I atoms also, we judge the overall success of vibration-to-electronic excitation transfer prospects for these atoms to be far less encouraging than originally predicted. New data from other researchers also support the conclusion that the rates for such transfer are in general not fast.

It is viewed that the transfer of vibrational energy to atomic excited states is unlikely to be very effective in general. The transfer to diatomic electronic states may be more promising. One problem has been identified as an important case to study - the possible transfer of excitation from $HF(v=3)$ to $CN(A)$ state.

In addition to our investigations of vibration-to-electronic excitation transfer, we have taken a second approach to the development of lasers useful for ARPA/ONR needs. We have identified a potentially very efficient and scalable new laser, on the $B^3\Sigma_u^- - X^3\Sigma_g^-$ transition of the molecule S_2 . The lasing action from 365-570 nm was first achieved by pumping with another laser. Because of fortuitous conditions involving the electronic states of S_2 , the molecule holds much promise for more direct, efficient excitation schemes. We recommend that we increase our research efforts on S_2 and similar species. Among the possible vibration-to-electronic transfer experiments, the highest priority should be placed on diatomic electronic laser candidates, and lowest priority on atomic candidates.

Technical Report

The goal of this research is to determine the potential effectiveness of using vibration-to-electronic (V-E) energy transfer to produce electronically excited lasing states. In general, not enough is known about V-E energy transfer to successfully predict or produce V-E transfer lasing. The concept is extremely attractive, if attainable, because there are numerous electrical and chemical sources of highly vibrationally excited molecules. Lasers based on V-E transfer processes may be highly efficient and scalable. Thus attempts to make accurate rate measurements are valuable at this time.

In some sense, V-E transfer lasers have been attempted long before an adequate understanding of these processes. Solomon and Blauer (Bell Aerospace) have been attempting to utilize the $H_2(v) + I \rightarrow H_2(v-2) + I^*$ transfer process to attain lasing on I^* for several years.¹ The bright emission from CN(A) in the $HF(v) + CN$ systems (Betts-TRW) may in fact be a V-E transfer type process.² If such a transfer laser on CN(A) is established, the importance of V-E transfer must be studied more closely.

As was outlined in our first proposal, at the start of this research, there are no inherent limitations to the principle of using V-E transfer to pump lasing electronic states.³ Yet it was pointed out that only under fortunate kinetic circumstances is it possible to generate new lasers. The main difficulty being the possibly small cross sections for transfer of multi-quanta of vibrational excitation to a single electronic state. In cases where V-E transfer to the appropriate state might occur, it would be even more difficult to find conditions where simultaneous transfer to lower laser levels did not occur.

Since the Northrup group has been investigating the possibilities for

V-E transfer in some molecular systems, it was deemed advisable for our effort to take on the directions of studying atomic electronic states. It was also considered to be the wisest approach to study systems which may have the highest chances of an effective demonstration of the V-E principle. Thus we undertook to study initially systems that required only one or a few vibrational quanta to produce the desired electronic state. These systems involved N_2^+ , H_2^+ + Br and I atoms. There is a great amount of literature now involving the E-V transfer from Br^* and I^* ($^2P_{1/2}$) states.⁴⁻⁷ In many cases, the E-V transfer is essentially 100% efficient. In addition, there are several theoretical papers which study the concept of resonance between Br^* and H_2 , HD, and D_2 .⁸ Thus we have a strong predictive handle in these simple systems.

Our computations based on the best data available for the $H_2(v=1) + Br \rightleftharpoons Br^* + H_2(v=0)$ system indicate that a laser should be possible in Br^* (2.7 μ) based on this equilibrium. A generous loss of Br^* due to quenching by H_2 , without back E-V transfer, was assumed. Conditions of 15% of the H_2 in $v=1$ and $[H_2(v=1)] \gg [Br]$ should produce a population inversion in Br^* . More optimistically, as little as 5% of H_2 in $v=1$ may force the inversion.

A flowing discharge laser tube was set up to determine if lasing could be effectively demonstrated in a simple lab device (Fig. 1). Microwave discharge cavities produce 50 μ of Br atoms from Br_2 at each end of the laser tube. All of the flows are directed toward the center main pump-out. Additional gases such as mixtures of H_2 and He, H_2 , N_2 , and He, etc. are added in separate parts. Under conditions where all reagents were flowing satisfactorily and Br atoms properly produced, both pulsed and cw discharges were fired in the 1 meter laser tube.

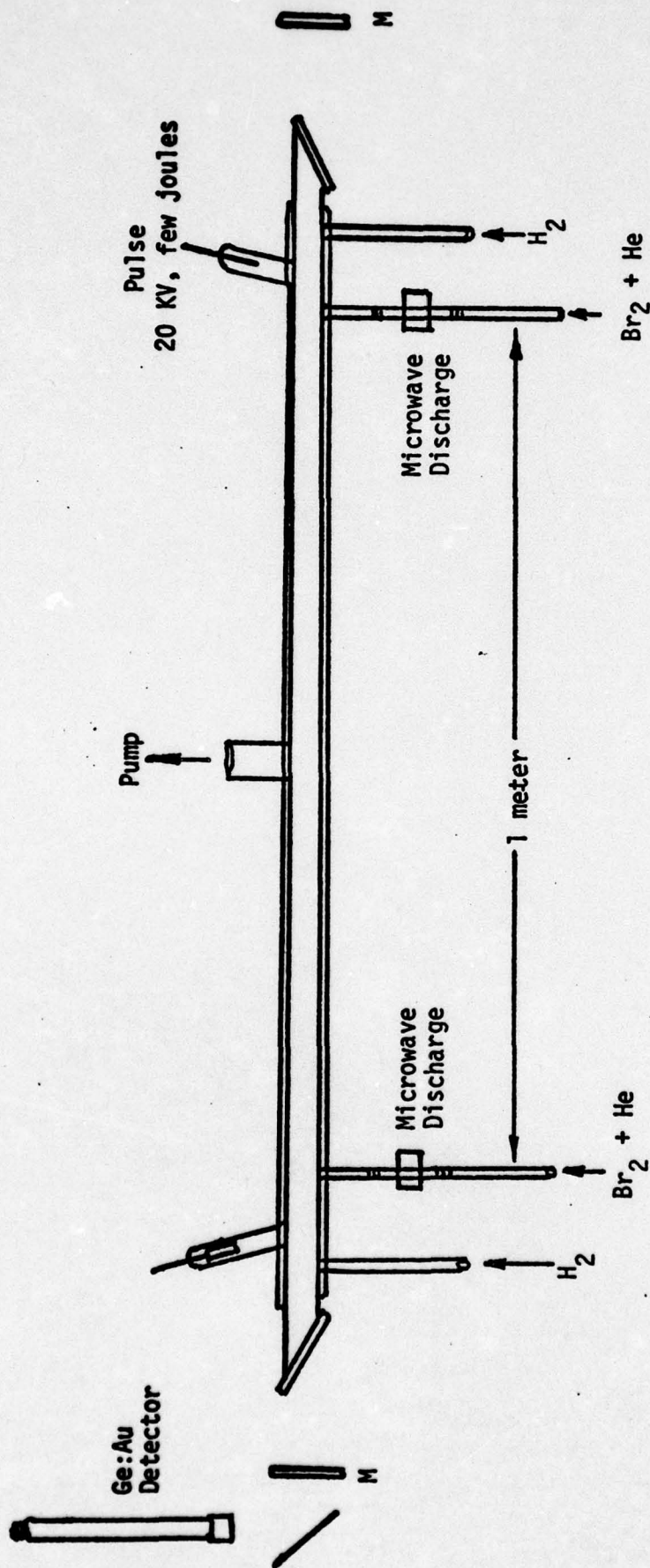
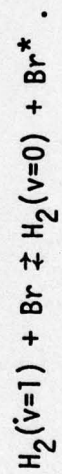


Figure 1. V-E transfer laser based on the system:



No lasing on Br^* was observed in this device. Continuous discharges from 10-20 kV and 20 mA and pulsed excitations of 4-20 joules at 15 kV were attempted. Gas mixtures consisted of typical pressures: 4 torr He, 4 torr H_2 (or 2 torr H_2 , 2 torr N_2), and 50 μ of Br. Stable cw discharges were difficult to obtain, but were achieved even with the addition of the Br.

The failure to achieve lasing could be due to a lack of significant excitation of the H_2 to ($v=1$). To further determine if this was the case, infrared emission was detected directly from Br^* in a discharge flow apparatus. Various vibrationally and electronically excited species were mixed directly into the Br atom flow and emission intensities detected. The results were most revealing:

Table I
Emission Intensities of Br^*

Discharge Excited Species	Relative Intensity
He	20
Ar	0
N_2	40
H_2	5

Excitations of Br^* , presumably by V-E transfer from $\text{H}_2(v=1)$ is far weaker than from either He or N_2 . Since He has no vibrational levels, a more plausible mechanism for Br^* excitation is electronic-to-electronic transfer from a high-lying metastable level of He, followed by radiative cascade in the Br system (Fig. 2). The energy mismatch between Br^* and

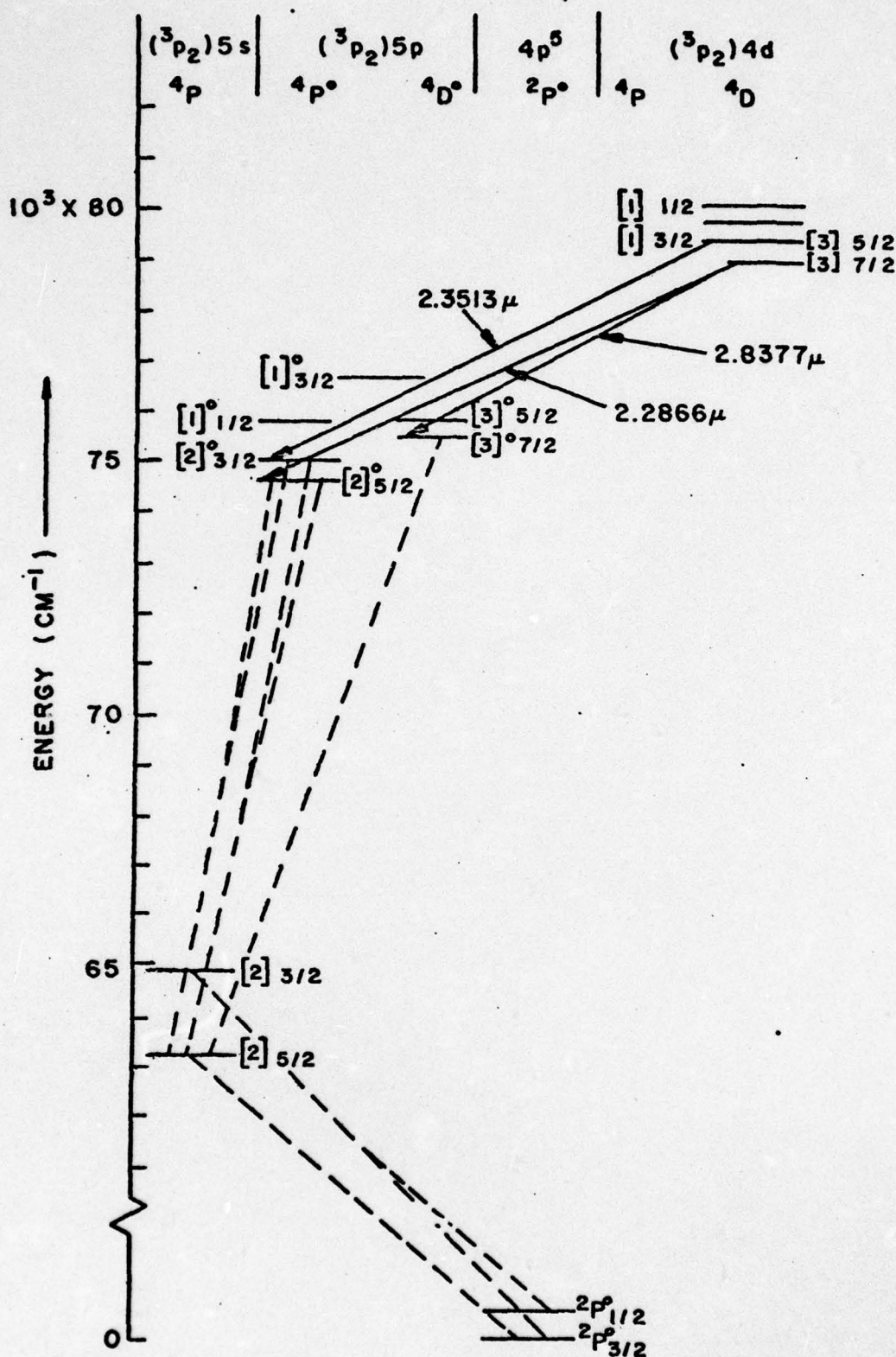


Figure 2. Energy level diagram for Br atoms, showing atomic laser transitions (solid arrows) and strong radiative lines (dotted lines). A pathway to the metastable $2p_{1/2}^\circ$ level exists from high-lying electronic states by E-E transfer followed by radiative cascade.

both $N_2(v=1)$ and $N_2(v=2)$ is large, thus V-E transfer is probably not the mechanism of excitation there either. We conclude that a similar E-E process from the $N_2(A^3\Sigma_u^+)$ state followed by radiative cascade is most likely responsible for the excitation. Conclusions with regard to the $H_2(v=1) + Br$ system must follow one or both of the explanations: (1) The H_2 molecules are not appreciably excited to $(v=1)$ in our discharge. (2) The $H_2(v=1) + Br \rightleftharpoons Br^* + H_2(v=0)$ equilibrium is not established to the extent expected. That is, more Br^* is lost by pure quenching (E-T,R) than by E-V back transfer.

Since these experiments were particularly illuminating, it seemed valuable to look also at I^* emission. The role of E-E transfer was pointed up so well with Br^* that emission results must be regarded with particular caution. E-E transfer has actually been the mechanism in many systems which were once thought to be V-E transfer ($N_2(v) + Na$, etc.).^{9,10} More recent evaluations of $Na^* + N_2$ have found very small cross sections for resonant E-V, V-E transfer.¹¹ The importance of the role of V-E transfer in the observed emission spectra of numerous species may be less than initially thought.

In the I, I^* system, the signal-to-noise advantage is much greater than for Br^* . However, under all the conditions tried, no emission was observed from I^* (1.3μ). This may be the result of two failures: the failure of any vibrationally or electronically excited species to transfer to the I atom, or the failure to generate I atoms in sufficient concentrations. The latter problem is a significant one, since we did not have an adequate means of checking for I atoms. I atom recombination on walls is particularly severe without proper coatings. Thus we must term this particular experiment as inconclusive at this time. However, under other

situations where I^* should have been observed by V-E transfer from $HF(v=2)$, none was detected.¹² This bodes badly for the chances of a V-E transfer laser in the I^* system if these results are true.

At the conclusion of these initial studies, we felt it unwise, in our best scientific judgment, to continue the search for V-E transfer in atomic systems. New data was becoming available on E-V transfer, from which cross sections for the reverse V-E transfer could be obtained. In the $Na^* + N_2$ system, for example, the V-E back transfer processes do not look promising.¹¹ The results cannot be generalized, however, because new evidence has been found, for example, on near-resonant E-V transfer in $Cs + H_2$.¹¹ We judge the system that would be most beneficial to study is the $HF(v=3) + CN$ transfer to the $CN(A)$ state. Further work on the atomic systems has presently been stopped.

In the course of this work, we have also reconsidered the basic approach or methodology of our efforts. Since V-E transfer measurements are difficult to do, and no single V-E transfer laser candidate has been identified as yet, it is difficult to determine where the greatest impact can be made with rate measurements. An alternate approach might be to identify some new candidate laser systems, which might operate comfortably and efficiently in scalable gas systems on visible or ultraviolet transitions. Our first approach in this regard was ultimately more successful.

The S_2 molecular system exhibits strong visible and ultraviolet emission in all kinds of flames, discharges, shock tubes, etc.^{13,14} The transition responsible for this emission is the $B^3\Sigma_u^- - X^3\Sigma_g^-$ (Fig. in appendix). Since the molecule emits strongly to high vibrational levels in the ground state, it has several built-in advantages. High efficiency is possible, because excessive excitation is not needed to reach the B

state. The high vibrational levels of the ground state are not significantly populated under any conditions of temperature, and they can most likely be relaxed readily to prevent bottlenecks. Vibrational levels less than $v' = 10$ in the excited state are not predissociative, thus excited molecules can be stored and losses are only due to collisional quenching.

Our first experimental effort to study the potential merit of the S_2 system for ARPA/ONR goals took the form of optical pumping with other lasers - a doubled dye laser and a nitrogen laser. Eventually the results of these experiments would allow an identification of possible alternate (direct) pumping schemes or energy transfer excitation.

Lasing action has been achieved in the S_2 ($^3\Sigma_u^- - ^3\Sigma_g^-$) system from 365-570 nm. As anticipated, the molecule has high gain and extremely good prospects for high efficiency. A preprint outlining the major aspects of the lasing characteristics is attached as an appendix to this report. The initial phase of optical pumping experiments is essentially complete, and work is about to begin on more direct pumping schemes. There are a number of distinct possibilities which we do not deem appropriate for discussion in this report now. To summarize this last effort, a working visible and ultraviolet laser has been achieved on S_2 ($^3\Sigma_u^- - ^3\Sigma_g^-$) and the prospects for efficient, direct excitation mechanisms look good.

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Appendix

A Tunable Visible and Ultraviolet Laser on S_2 ($B^3\Sigma_u^- - X^3\Sigma_g^-$)

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Abstract

A new laser has been achieved on the $B^3\Sigma_u^- - X^3\Sigma_g^-$ transition of S_2 by optical pumping with a frequency doubled dye laser and a nitrogen laser. The observed lasing lines are tunable from 365 nm to 570 nm. The S_2 molecule is a promising candidate for an efficient, scalable ultraviolet laser system.

There is widespread interest in the development of efficient, tunable visible and ultraviolet lasers. We have achieved lasing in a promising new molecular system, the sulfur dimer, S_2 , on its $B^3\Sigma_u^- - X^3\Sigma_g^-$ transition. Emission from the $S_2(B-X)$ is widely observed in flames, shock tubes, and discharges whenever compounds of sulfur are present.^{1,2} In this first demonstration of the lasing characteristics of S_2 , line tunable laser action is observed from 365 nm to 570 nm by pumping with a frequency doubled dye laser. Initial results indicate that the S_2 laser is highly efficient, scalable, nondegradable, and offers strong promise for successful pumping by other excitation schemes.

A report of an S_2 laser on the $^1\Sigma_g^+ - ^3\Sigma_g^-$ transition at 1.1 μm has been made.³ The S_2 laser considered here lases on a different transition. Figure 1 sketches the approximate potential surfaces for the known S_2 molecular states.⁴ Although many details about these surfaces and the exact locations of other states are not known, several qualitative features of these potential surfaces are most important. All of the lasing states explored in this study, including $v' = 2, 3, 4, 5, 6, 7$, are well below the dissociation limit of the S_2 molecule. Thus, the lowest vibrational levels of the $B^3\Sigma_u^-$ state, although heavily perturbed, are not predissociated.⁵⁻⁸ The potential surfaces are fortuitously situated so that any small population in $v' \geq 0$ of the $B^3\Sigma_u^-$ excited state is inverted with respect to the high vibrational levels of the ground $X^3\Sigma_g^-$ state. The Franck-Condon factors for these B-X transitions are as large as 0.1 for many bands and cover broad spectral ranges before diminishing.⁹ The measured fluorescence lifetimes of individual states is approximately 20 nsec, giving $A_{v',j}^{v'',j''}$ coefficients for single lines on the order of 10^5 to 10^6 sec^{-1} .^{9,10} Thus in the experiments described here, high gain laser

action from a single rotational level in $v' = 5$ was observed on numerous lines over a 365 nm to 530 nm range. Wavelength regions which are missed because the Franck-Condon factors drop to zero at the nodes of one upper state vibrational wave function are conveniently covered by the next higher and lower vibrational levels. Thus taking into account that successive vibrational bands nearly overlap, and the availability of numerous sulfur isotopes, almost complete coverage of the ultraviolet and visible regions of the spectrum is possible.

The experimental setup for generating S_2 molecules consists of a 12-cm long Brewster angle, all fused quartz cell. The cell is evacuated with a few milligrams of sulfur inside, sealed off, and housed in a 500°C tube furnace. Such sealed-off cells have operated successfully without degradation for several months. The vapor pressure of sulfur inside the cell is adjusted between 1 and 10 torr with a sidearm maintained at 180-240°C. At temperatures above 500°C and at these low vapor pressures, the large ring molecules of sulfur break down, to give predominantly sulfur dimers.¹¹ Initial experiments were accomplished with a nitrogen laser pump (1-10 mJ per pulse, 10 nsec). The pump laser is focused through a partially transmitting input mirror longitudinally into the S_2 cell. The S_2 laser mirrors are typically 99% R and 50% R over the visible or ultraviolet range desired. The nitrogen laser, 337.1 nm, overlaps with the (2,4) band of S_2 .¹² At a pressure of ~10 torr, bright spontaneous fluorescence from the side is visible, even with the room lights on, when the nitrogen laser excites the S_2 . Stimulated emission was first observed in the blue region of the spectrum. Our previous calculations fully anticipated high gain lasing on S_2 with this short pulse excitation.

In more recent and refined experiments, the S_2 laser was pumped in a similar fashion with a frequency doubled dye laser. This provided the advantage of tuning the pump laser over a variety of bands absorbing from 290 nm up to 305 nm. Bands were excited from the (3,0) to (7,0).¹² The dye laser has characteristic pulsed energies in the ultraviolet of 0.5 mJ, 0.5 cm^{-1} bandwidth using a low finesse ($R=30\%$) etalon, and 2 μsec duration. The peak power with the dye laser is considerably lower than for the nitrogen pump. Most stable lasing was achieved when the dye laser was focused to a beam radius of a hundred microns in a few torr of S_2 .

All bands that were pumped by the doubled dye laser exhibited strong lasing action throughout the visible. The lasing wavelengths were primarily in the violet, blue, blue-green, and green regions, centered about the reflectivity maximum of the mirrors, 450-550 nm. The strongest observed laser lines correspond well with the wavelengths of emission bands recorded in Rosen for each S_2 band pumped. Sharp P and R branch doublets are observed for each lasing transition. For a single pump wavelength, as many as 8-10 doublets, spaced by the vibrational levels in the ground state, lased simultaneously in the broad band cavity. Lasing was observed both with and without narrowing of the pump bandwidth. More powerful and stable operation was achieved with modest narrowing to 0.5 cm^{-1} . Experimentally the pump energy needed for threshold in the S_2 laser with the 50% output coupler was 100 μJ . The pump band however is ten times broader than individual S_2 lines, and much of the pump light was not being used to produce the lasing state. Gain was observed to be superfluorescent on the strongest lines at higher S_2 pressures. Transitions as short in wavelength as 400 nm and as long as 570 nm

were observed to lase, where both mirrors had a reflectivity of only 50%. A cavity composed of $R = 99\%$ at 360-410 nm and $R = 40\%$ at 350-400 nm mirrors sustained stable and strong lasing at wavelengths observed from 365 nm to 390 nm. In this setup the strongest visible lines were not completely suppressed. Energy conversion was measured for the total visible output of the S_2 laser and was found to be 2%.

Each S_2 band is 15-25 Å wide in absorption, and tuning has been accomplished over entire bands. Typically there are strong S_2 absorption lines every few cm^{-1} in a single vibrational band. However, there are numerous rotational satellites and overlapping bands. In practice, 3-4 lasing absorptions are observed per cm^{-1} . In regions of the band heads, the spectrum is even more dense. The pump laser was tuned over numerous lines in the (5,0) band, and the lasing output tuned correspondingly within the (5,21) band which was observed in the monochromator. With the numerous isotopes of sulfur available, almost any desired wavelength can be attained.

From a number of considerations, the optically pumped S_2 laser described here is not fully optimized. As mentioned, the pump wavelength is a factor of ten times broader than the S_2 lines. Proper mode matching of the focused pump beam to the S_2 laser cavity has not been attempted. The present conditions utilize 3m radius of curvature mirrors, which sustain a beam area inside the cavity an order of magnitude larger than the pump zone. Bright spontaneous emission is observed from the side of the S_2 cell because of the short radiative lifetime. Even when the best lasing was obtained, this emission was not dramatically reduced in intensity. We anticipate that more proper mode matching will greatly

enhance the output. In these first experiments, also, the laser gain length was restricted to the 12 cm cell. The laser operation was observed to fall off abruptly with increased pressure. Most likely S_2 - S_2 collisions are quenching the $B^3\Sigma_u^-$ state. Operation with a longer path length and lower total S_2 pressure should greatly improve the conversion efficiency. Since only lasing transitions which originate from a single excited state are observed, most likely any molecules which are relaxed result in excitation which is lost from the system for laser output. Experiments are in progress to test whether some selective relaxation by addition of other molecules or rare gases can enhance the efficiency or tuning range without quenching. The S_2 laser pulse in our system follows precisely the entire time duration and shape of the 2 μ sec doubled dye laser pulse. However relaxation effects will be important to determine whether bottlenecks occur in the ground state lasing levels.

The sulfur laser compares very favorably to the other optically pumped molecular dimer systems, I_2 ,¹³ Na_2 ,¹⁴ and Br_2 .¹⁵ With fully optimized parameters, conversion efficiencies should far exceed the 2% measured here. It is likely that other pump sources such as the XeF laser or single line high power arc lamps⁹ may be suitable to excite the S_2 molecule. Since strong $S_2^3\Sigma_u^-$ emission has been observed under numerous other conditions, it is likely that chemical or electrical pumping schemes are possible also. The ease with which the sulfur dimer appears to be formed in the appropriate excited state warrants further investigation of S_2 as an efficient and tunable visible and ultraviolet laser source.

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Figure Caption

Figure 1. Approximate known potential surfaces for the S_2 molecule (Ref. 4).

The levels $v' \leq 9$ are bound, but often perturbed. They are characteristic strong emitters. The levels $v' \geq 10$ are not observed in emission, probably due to strong predissociation. One pump excitation line and the maximum and minimum observed lasing wavelengths are shown for $v' = 5$. Lasing transitions are also observed to almost all v'' levels in between, whenever the Franck-Condon factors are not nearly zero.

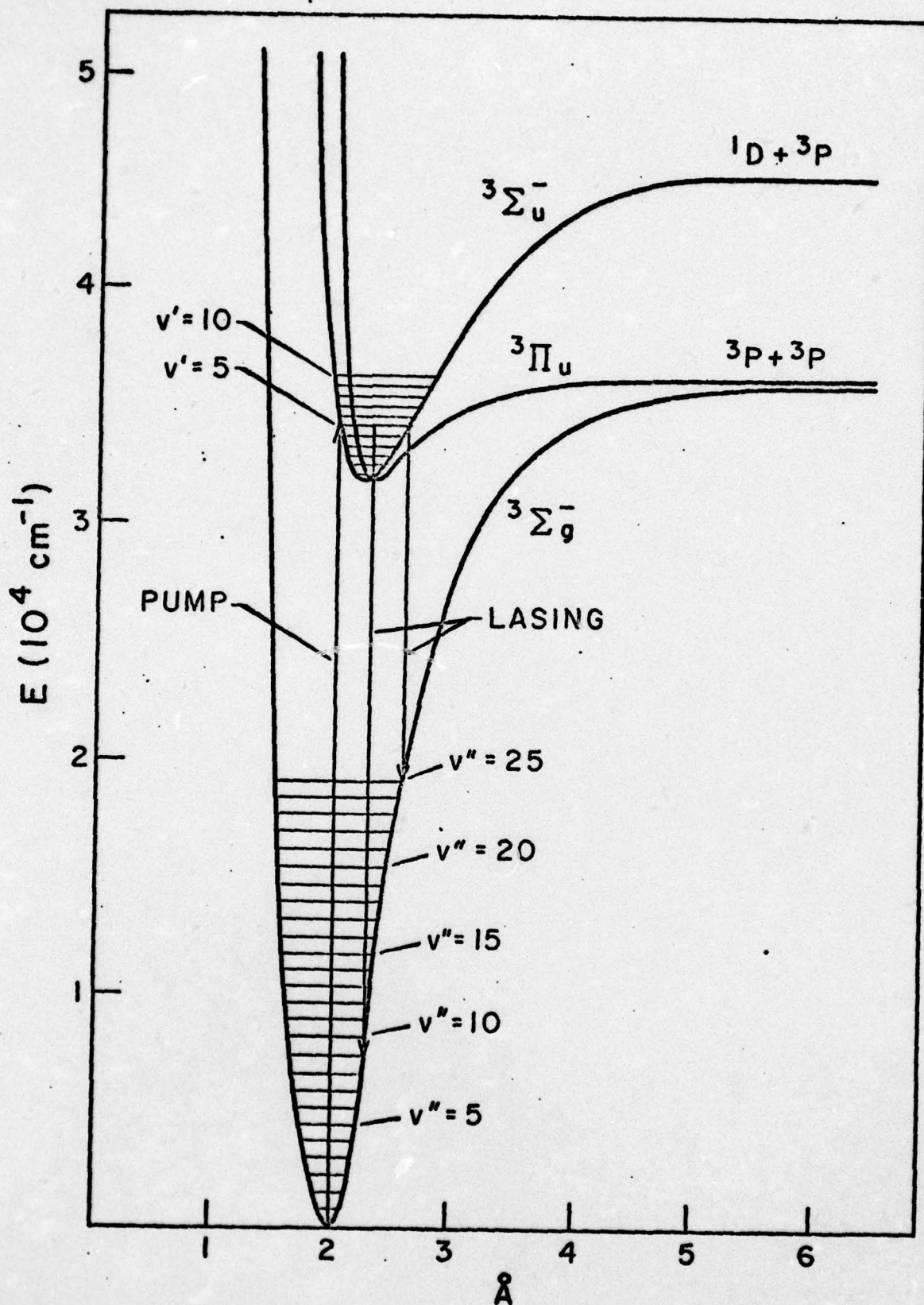


Figure 1